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SPECIFICATION

COLLECTOR FOR STORAGE BATTERY, STORAGE BATTERY COMPRISING
THE SAME, AND PROCESS FOR THE PRODUCTION THEREOF

<Prior Art>

The present invention relates to a collector for storage battery, a storage battery comprising same and a process for the production thereof.

<Background Art>

The material constituting a positive collector is required to have a high electrical conductivity, a high insolubility in electrolyte, a high chemical stability at a positive electrode potential in electrolyte, a high hydrogen overvoltage, a high oxygen overvoltage, and so on. When exposed to positive electrode in an electrolyte, carbon or an inexpensive metallic material having a light weight such as aluminum is vigorously dissolved or corroded. Thus, these materials cannot be used. Most metallic materials cannot be used for the reason that they are corroded or dissolved. Among ceramics such as oxygen compounds or silicon compounds, there can be found a few corrosion-resistant electrically-conductive materials

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(e.g., SnO_2 , TiSi_2 , Ti_5Si_3 , TaSi_2 , TaSi_3 , NbSi_2 , Nb_5Si_3 , and so on).

Although these electrically-conductive ceramic materials have an excellent electrical conductivity (volume resistivity: $1 \Omega\cdot\text{cm}$ or less), they have a high resistivity and require a high cost as compared with metallic materials (volume resistivity: 10^{-6} to $10^{-5} \Omega\cdot\text{cm}$ or less). Therefore, these electrically-conductive ceramic materials cannot be used as collector as they are. However, by forming a thin layer of this electrically-conductive ceramic on the surface of a collector to coat the collector substrate, the voltage drop due to this electrically-conductive ceramic can be minimized, making it possible to overcome the problems of resistivity and cost and hence obtain a positive collector excellent in corrosion resistance. Some electrode systems wherein an electrically-conductive ceramic is coated based on this idea have been reported.

Example.: *Denki Kagaku* (Electrochemistry) 47, 668 (1979), 48, 384 (1980)

Ti (substrate)/ SnO_2 (doped with Sb)/ $\beta\text{-PbO}_2$

Ti (substrate)/ $\text{PtOx}/\beta\text{-PbO}_2$

Ti (substrate)/ $\text{IrO}_2/\beta\text{-PbO}_2$

Ti (substrate)/ $\text{RuO}_2/\beta\text{-PbO}_2$

An actual example of such an electrode coated with such an electrically-conductive ceramic is a lead dioxide electrode used as DSA electrode for electrolysis.

Example: JP-A-63-57791 (The term "JP-A" as used herein means an "unexamined published Japanese patent application")

Ti (substrate)/platinum/ α -PbO₂/ β -PbO₂ ... DSA electrode produced by Permelec Electrode Ltd.

Referring to the reason why these electrodes comprise Ti as a substrate, using a conventional dip coating method, a process called calcination, which is accompanied with the rise of the temperature of the substrate to around 500°C, is required to scatter an organic metal and to provide the thin film material with a good crystallinity and electrical conductivity, since the formation of the thin layer needs a liquid phase as a medium. Even a spray heat decomposition method involving the deposition from a liquid phase which is widely used mainly on an industrial basis requires a process for raising the substrate temperature to about 340°C at lowest. Thus, a corrosion-resistant thin layer having good characteristics cannot be formed on the surface of the substrate unless a collector made of a material having a high melting point such as Ti is used.

However, such a positive collector using Ti or any other high melting metals as a material is disadvantageous in that it finds difficulty in working or welding of electrode plate for the preparation of storage battery, adding to the assembly cost.

Ti is also disadvantageous in that when exposed to positive electrode potential in an electrolyte, it is anodized and passivated in a short period of time, making it impossible for the collector substrate to maintain its function as collector if the electrolyte penetrates into the interface of the collector substrate with the coat layer. Further, the conventional film-forming method involving the deposition from a liquid phase is disadvantageous in that since the adhesivity between the coat layer and the substrate is small and the coat layer is liable to much defects such as cracking, the electrolyte penetrates into the interface of the coat layer with the substrate through cracks in the coat layer to cause anodization of the surface of the substrate, making it impossible to keep the collector resistant to corrosion. Accordingly, it is necessary that the coat layer of electrically-conductive material thus formed be subjected to post-treatment such as plating with β -PbO₂.

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The inventors paid attention to and confirmed the fact that the use of sputtering method or plasma CVD method among today's diversified methods for forming a thin film makes it possible to coat an inexpensive low melting material which can be easily worked such as lead with a high melting electrically-conductive ceramic having a good crystallinity and electrical conductivity such as SnO_2 . This surface treatment made it possible to drastically enhance the corrosion resistance of positive collector. It was made obvious that the thin film formed by such a film-forming method is extremely resistant to defects such as cracking and exhibits a far greater adhesivity to the substrate than that prepared by the conventional film-forming method involving the deposition from a liquid phase, eliminating the necessity of extra post-treatment such as plating with $\beta\text{-PbO}_2$ as conventionally practiced.

Basically, the surface-treated collector described in the invention can be effectively applied to various battery systems. A lead acid battery, for example, has long been used as a secondary battery from the standpoint of cost, safety and reliability but is disadvantageous in that it has a low energy density as compared with new types of batteries which have shown improvements in

performance and been spread in recent years (nickel-metal hydrogen, Li-ion, and so on).

The reason for this disadvantage is that the lead acid battery has a low theoretical energy density. In addition, lead constituting the positive electrode plate in the lead acid battery gradually corrodes to deteriorate to lead dioxide with time in operation. Therefore, more than a predetermined volume of collector needs to be secured to meet the requirements for life properties. This adds to the thickness and weight of the electrode plate.

Further, when the thickness of the electrode plate is raised, the electrolyte can penetrate deep into the electrode plate less fairly, lowering the percent utilization of the active material. It is known good to lower the specific gravity of the electrolyte for the purpose of improving the corrosion resistance of the positive collector. This practice, too, worsens the diffusion of the electrolyte, causing the drop of the percent utilization of the active material. When the percent utilization of the active material is lowered, the active material is needed more to draw a required amount of electric capacity, adding to the weight of the electrode plate and hence further lowering the energy

density. Thus, the necessity of countermeasuring against the corrosion and deterioration of the positive collector causes further reduction of the actual energy density of a lead acid battery having a low theoretical energy density.

As mentioned above, the use of a collector coated with an electrically-conductive ceramic makes it possible to eliminate the necessity of using a collector substrate which is heavier than required and withstand the use of an electrolyte having a high specific gravity. Accordingly, the practical energy density can be drastically enhanced.

Unlike the conventional lead acid battery, however, the collector surface-treated with an electrically-conductive ceramic does not undergo chemical bonding reaction with an active material at the ripening step. Thus, the resulting adhesivity between the collector and the active material is deteriorated. Accordingly, some physical force such as gas production during charging, expansion and shrinkage of active material accompanying charging and discharging and external vibration can cause the collector and the active material to be separated from each other, disabling the collector from performing as an electrode plate.

In order to enhance the energy density of the battery, the specific gravity of the electrolyte can be

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raised. Further, the percent utilization of the active material can be enhanced by reducing the thickness of the electrode plate and improving the diffusibility of the electrolyte. This can be accomplished by the use of a collector having a drastically improved corrosion resistance. However, it is apprehended that when the thickness and volume of the collector are reduced to reduce the weight of the battery, the sectional area of the portion through which electric current flows is reduced, causing the rise of voltage drop due to the resistivity of the collector and hence causing the active material to be used unevenly to lower the percentage utilization of the active material or have other adverse effects on discharge properties.

Further, when the size of storage battery is increased, the strap or pole through which electricity flows between the electrode plate and the terminal, too, have a larger size that adds to the weight of the battery.

*Just
thick* The present invention has been worked out under these circumstances. The modern technique for the production of thin film was used to coat a collector substrate with a thin film of electrically-conductive ceramic having a high adhesivity and hence provide the collector with an improved corrosion resistance. In this

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manner, the use of an electrolyte having a high specific gravity is made possible while suppressing the rise of the weight of the collector, resulting in the enhancement of the percentage utilization of the active material and hence making it possible to realize a storage battery having a prolonged life and a high energy density.

Further, by providing a structure such that a collector having an active material provided on the surface thereof is pressed in the direction perpendicular to the surface thereof at a predetermined pressure to maintain electrical contact and the surface of the collector free of acting material forms a part of the battery outer case to act as collector, battery outer case and connecting terminal at the same time, strap or pole can be omitted from the storage battery. Accordingly, an inexpensive high performance storage battery having a high reliability which requires no additional weight and cost of strap or pole, undergoes no abnormal corrosion and can be produced in a simple manner and a process for the production of such a storage battery can be provided.

~~<Disclosure of the Invention>~~

The collector for storage battery according to the present invention has the following characteristics:

- (1) A thin electrically-conductive ceramic layer is formed on the surface of a collector substrate.
- (2) A process involving the deposition from a gas phase is used to form the foregoing thin electrically-conductive ceramic layer on the surface of a collector substrate.
- (3) The foregoing process involving the deposition from a gas phase is sputtering process.
- (4) The foregoing process involving the deposition from a gas phase is plasma CVD process.
- (5) The material constituting the foregoing collector substrate is a metal or metal alloy selected from the group consisting of lead, lead alloy, tin, tin alloy, bismuth and bismuth alloy.
- (6) The material constituting the foregoing collector substrate is an electrically-conductive polymer.
- (7) As the foregoing electrically-conductive ceramic there is used SnO_2 .
- (8) The foregoing electrically-conductive ceramic SnO_2 comprises an Sb compound incorporated therein in an amount of from 0.5 mol-% to 8 mole % based on the total amount of moles of Sn and Sb.

(9) The foregoing electrically-conductive ceramic SnO_2 comprises F incorporated therein in an amount of from 7 mole % to 60 mole % based on the total amount of moles of Sn and F.

(10) As the foregoing electrically-conductive ceramic, any silicon compound selected from the group consisting of TiSi_2 , Ti_5Si_3 , TaSi_2 , Ta_5Si_3 , NbSi_2 and Nb_5Si_3 is used.

The storage battery comprising such a collector has the following characteristics:

(11) A lead acid battery comprising a collector for storage battery according to any one of (1) to (9).

(12) A lead acid battery comprising a collector for storage battery according to (10).

(13) A storage battery comprising a collector for storage battery according to any one of (1) to (10), characterized in that the collector has an active material provided thereon and there is provided a structure such that a pressure of 4×10^4 to 20×10^4 Pa is maintained perpendicular to the surface of the collector.

(14) The storage battery according to (13), comprising a bipolar battery type structure comprising a plurality of bipolar type electrodes

each comprising a positive active material provided on one side of a collector for storage battery and a negative active material provided on the other side, wherein the positive active material side of one bipolar electrode being opposed to the negative active material side of another, and a separator for retaining an electrolyte provided between said laminated bipolar type electrodes.

(15) The storage battery according to (13), comprising one or two collectors for storage battery having an active material provided on one surface thereof but free of active material on the other surface, wherein the surface of the collector which is free of active material forms at least a part of the outer case of the storage battery.

The process for the production of a storage battery according to the invention has the following characteristics:

(16) A process for the production of a lead acid battery according to (11), characterized in that formation begins within a period of time T (minute) represented by the following equation after the injection of an electrolyte depending on the

thickness of the coat layer of electrically-
conductive ceramic (A μm):

$$T \text{ (min.)} \leq 19.2 \log_{10} A \text{ (}\mu\text{m)}$$

(17) The process for the production of a lead acid battery according to (16), wherein the electrode plate is subjected to formation with the battery voltage being controlled to 1.0 V/cell or more within T minutes after the injection of the electrolyte.

(18) The process for the production of a lead acid battery according to (16) or (17), wherein the electrode plate is subjected to formation with the battery voltage being controlled to 1.0 V/cell or less for at least 1 hour after the beginning of formation.

(19) A process for the production of a storage battery comprising a collector for storage battery according to (6), characterized in that the collector is heat-fused to a plastic battery outer case.

<Brief Description of the Drawings>

Fig. 1 is a schematic diagram illustrating a section of a positive collector according to the invention;

Fig. 2 is a characteristic diagram illustrating the relationship between the amount of Sb incorporated in thin SnO_2 layer and the resistivity of SnO_2 layer;

Fig. 3 is a characteristic diagram illustrating the relationship between the amount of F incorporated in thin SnO_2 layer and the resistivity of SnO_2 layer;

Fig. 4 is a characteristic diagram illustrating the relationship between the thickness of thin electrically-conductive ceramic layer and the maximum allowable resistivity;

Fig. 5 is a characteristic diagram illustrating the transition of the terminal voltage during oxidation test;

Fig. 6 is a characteristic diagram illustrating the corroded amount of Pb electrode after oxidation test;

Fig. 7 is a characteristic diagram illustrating the discharge characteristics;

Fig. 8 is a schematic sectional view illustrating an embodiment of the structure of a lead acid battery comprising an electrically-conductive ceramic as a positive electrode;

Fig. 9 is a characteristic diagram illustrating the transition of discharge capacity during cycle life test;

Fig. 10 is a schematic sectional view illustrating an embodiment of the structure for the enhancement of the voltage of a lead acid battery comprising an electrically-conductive ceramic as a positive electrode;

Fig. 11 is a schematic sectional view illustrating an embodiment of the structure for the enhancement of the capacity of a lead acid battery comprising an electrically-conductive ceramic as a positive electrode;

Fig. 12 is a schematic sectional view illustrating the structure of a bipolar lead storage battery comprising an electrically-conductive ceramic as a positive electrode;

Fig. 13 is a characteristic diagram illustrating the relationship between the limit forming voltage and the amount of PbO_2 after formation;

Fig. 14 is a characteristic diagram illustrating the relationship between the limit forming voltage and the thickness of corroded layer after oxidation test;

Fig. 15 is a characteristic diagram illustrating the relationship between the time required until formation begins after the injection of an electrolyte and the thickness of corroded layer; and

Fig. 16 is a characteristic diagram illustrating the limit of the thickness of SnO_2 layer which is not dissolved and the time required until formation begins.

In the foregoing diagrams, the reference numeral 1 indicates a positive collector substrate, the reference numeral 2 indicates an electrically-conductive ceramic, the reference numeral 3 indicates a positive active material, the reference numeral 4 indicates a negative collector, the reference numeral 5 indicates a negative active material, the reference numeral 6 indicates a separator, the reference numeral 7 indicates an exhaust port, the reference numeral 8 indicates a plastic battery outer case, the reference numeral 9 indicates a ~~connecting~~ ^{terminal} plate, and the reference numeral 10 indicates a bipolar electrode.

<Best Mode for Carrying Out the Invention>

The present invention will be further described hereinafter with reference to the following Examples.

[Example 1]

Fig. 1 is a diagram illustrating a section of the positive collector according to the invention. The reference numeral 1 indicates a collector substrate made of lead, which is a low melting metal. The reference numeral 2 indicates an electrically-conductive ceramic

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(SnO_2). The formation of the thin layer was carried out using a target made of the same composition as that of the thin layer to be formed (SnO_2) in an Ar gas atmosphere at a pressure of 0.75 Pa in an RF sputtering apparatus. The temperature of the substrate during film formation was 120°C , which is sufficiently lower than the melting point of lead (327°C). In the present Example, as the substrate there was used lead. However, even a material which has a low melting point and thus has heretofore been considered difficult to be coated, such as lead alloy, tin, tin alloy, bismuth and bismuth alloy was used to obtain a collector having the same structure as with lead.

Fig. 2 is a diagram illustrating the results of measurement of the resistivity of the thin layer thus formed. It is clear that, the layer of SnO_2 having Sb incorporated therein exhibits a lowered resistivity. When the content of Sb fell within the range of from 0.5 to 8 mole % based on the total amount of moles of Sn and Sb, a good layer having a small resistivity was obtained.

Fig. 3 is a diagram illustrating the results of measurement of the resistivity of a thin layer made of SnO_2 having F incorporated therein instead of Sb. It is clear that the layer of SnO_2 having F incorporated therein, too, exhibits a lowered resistivity. When the content of

F fell within the range of from 7 to 60 mole % based on the total amount of moles of Sn and F, a good layer having a small resistivity was obtained.

Fig. 4 is a characteristic diagram illustrating the results of examination of the relationship between the thickness and the maximum allowable resistivity of a thin layer. In this diagram, the results are shown under conditions such that the voltage drop at a current density of 100 mA/cm² is 1 mV or less. This current density corresponds to 1 CA (C: rated capacity) in a practical storage battery. If the voltage drop is 1 mV or less, there are little or no adverse effects on the discharge characteristics.

As can be seen in these diagrams, if the thickness of SnO₂ layer is 100 μm or less, there are no adverse effects on the battery properties. Further, the layer of SnO₂ comprising Sb or F incorporated therein causes less voltage drop. Therefore, the thickness of such a layer can be increased to reduce the occurrence of defects such as pinhole in the coat layer of electrically-conductive ceramic, making it possible to raise the reliability of the storage battery.

Lead and titanium were used as collector substrates. Some samples were used as electrode as they were. The

other samples were coated with a thin SnO_2 layer to a thickness of $15\text{ }\mu\text{m}$ by sputtering. These electrode samples were coated with a paste-like active material for lead acid battery, and then subjected to ordinary formation. As an electrolyte there was prepared sulfuric acid having a specific gravity of 1.280. These samples were then subjected to anodization test at a constant current of 20 mA/cm^2 . The transition of voltage during test is shown in Fig. 5.

The uncoated titanium substrate underwent passivation on the surface thereof and thus early showed a remarkably high resistivity that prevented itself from maintaining its electrode function. Ti electrode coated with SnO_2 showed no problems with voltage behavior even after 600 hours of oxidation test. When disassembled for examination after test, this electrode was found to have no deterioration in SnO_2 layer. On the other hand, the electrode made of Pb substrate didn't lose its function in a short period of time even if it was uncoated. However, when uncoated, lead as substrate underwent remarkable corrosion.

Fig. 6 is a diagram illustrating the corroded amount of the lead electrode measured after 600 hours of anodization test of Fig. 5. It is clear that the coated

lead electrode undergoes remarkably less corrosion than the uncoated lead electrode.

Fig. 7 is a diagram illustrating the discharge characteristics developed when the coated and uncoated electrodes comprising Pb as a collector substrate were discharged at various current densities. It is clear that there was no difference in voltage drop between coated Pb electrode and uncoated Pb electrode, i.e., change in the effect of resistivity of coat layer on voltage drop.

In the present Example, electrodes formed by sputtering SnO_2 onto the surface of Pb collector were used. Electrodes formed by sputtering any silicon compound selected from the group consisting of TiSi_2 , Ti_5Si_3 , TaSi_2 , Ta_5Si_3 , NbSi_2 and Nb_5Si_3 onto the surface of Pb to a thickness of 10 μm were also prepared and subjected to the foregoing test. Similarly to the case of coating with SnO_2 , these electrodes underwent little corrosion, demonstrating that these silicon compounds, too, have a remarkable corrosion-protecting effect. There was shown no difference in discharge characteristics between SnO_2 and these silicon compounds.

In the present Example, sputtering method was used. Technically, however, plasma CVD method can be used to obtain similar effect.

[Example 2]

The surface of a positive collector obtained by sputtering SnO_2 onto a Pb sheet having a thickness of 0.5 mm to a thickness of $10\text{ }\mu\text{m}$ was coated with a positive electrode paste for lead acid battery. A negative electrode was prepared by applying a negative electrode paste to an ordinary Pb sheet. The positive electrode and the negative electrode were combined with a glass mat separator for retainer type valve regulated lead acid battery provided interposed therebetween at various pressures. Using an ordinary method, sulfuric acid as an electrolyte was injected into the combination which was then energized (formed) to assemble a battery as shown in Table 1. Thus, a valve regulated lead acid battery having a capacity of about 0.25 Ah was prepared. In this battery, the surface of the both collectors free of active material forms a part of the battery outer case and also acts as a terminal from which current is drawn as shown in Fig. 7. For comparison, a conventional valve regulated lead acid battery using a Pb sheet free of SnO_2 layer was prepared and subjected to test.

Table 1: Test battery

Battery No.	Positive electrode plate	Pressure (kPa)	Remarks
A	Pb/SnO ₂ (10 μm) / active material (7 g)	20	Present invention
B		40	
C		100	
D		200	
E		400	
F	Pb/active material (7 g)	20	Conventional lead acid battery

These batteries were each subjected to charge-discharge cycle test, i.e., discharged with a current of 0.6 CA for 1 hour and then charged with a current of 0.2 CA for 4.1 hours at room temperature. The transition of discharge capacity during life test is shown in Fig. 8.

The life of the conventional valve regulated lead acid battery was expired after about 500 cycles. All the valve regulated lead batteries of the invention which had been prepared at a pressure of from 40 kPa to 200 kPa showed little or no capacity drop at 800th cycle. However, the cell A, which had been prepared at a low pressure (20 kPa), showed a capacity drop as very early as at 100th cycle. When disassembled, the cell A was found to have its positive active material peeled off from the collector. It is thus presumed that since the cell A had been prepared at a low pressure, the resistivity at the interface of the collector with the active material and

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the internal resistivity of the battery rose during test, lowering the capacity of the battery in early stage. The valve regulated lead acid battery E, which had been prepared at the highest pressure, i.e., 400 kPa, showed a capacity drop at 300th cycle. When disassembled, the cell E was found to have its active material penetrating into the glass mat, causing shortcircuiting. It is thus presumed that since the cell E had been prepared at too high a pressure, the particulate PbO_2 or Pb, which is an active material, penetrated deep into small pores in the separator.

As can be seen in the foregoing results, it is necessary that the positive electrode plate obtained by forming SnO_2 on the surface of a substrate made of Pb, and then applying an active material to the substrate be subject to a high pressure because it has a poor adhesivity between the collector having SnO_2 formed on the surface thereof and the active material as compared with the conventional lead collector free of SnO_2 coat layer used as a positive electrode which is oxidized on the surface of Pb substrate and thus undergoes chemical bonding to PbO_2 as a positive active material. It is also necessary that the pressure be limited to a range of from

40 to 200 kPa since, if it is too high, it causes shortcircuiting.

In the present Example, a positive electrode plate obtained by applying an active material to a collector was used. However, even when active material pellets which had been separately prepared were allowed to come in contact with a collector at a predetermined pressure, the same results were obtained.

In the present Example, SnO_2 was used for electrically-conductive ceramic, which is a corrosion-resistant coat. However, any other silicon compounds selected from the group consisting TiSi_2 , Ti_5Si_3 , Ta_5Si_3 , NbSi_2 and Nb_5Si_3 described in Example 1, too, exhibit a poor adhesivity to the active material and require the same pressure as required for SnO_2 .

In the present Example, 2V batteries as shown in Fig. 8 were prepared. As shown in Figs. 10 and 11, however, it is easy to prepare a module battery having a high voltage or capacity by laminating 2V batteries. This battery requires little or no time to weld or connect lead alloy parts on a block of electrode plates as required for the realization of conventional lead acid battery having a higher voltage. In this arrangement, the production cost and parts cost can be reduced. Further, since there

occurs no voltage drop at this connection portion, a high output can be obtained. At the same time, the weight of the connection portion can be reduced.

By using a technique involving the use of the electrically-conductive ceramic-coated collector as a positive electrode, a bipolar battery can be realized since such a collector does not basically corrode. A bipolar battery is a battery for high voltage use which can be prepared by applying positive and negative active materials to the respective surface of a collector, and then laminating a plurality of such electrode plates with a separator interposed therebetween as shown in Fig. 12. Such a battery comprising electrode plates each having both positive and negative active materials is called bipolar battery. Even this battery has heretofore exhibited a reduced life due to the corrosion of the positive collector. In order to prolong the life of this battery, the thickness and weight of the electrode plate must be raised, lowering the energy density. The connection of a plurality of cells has required much time to weld or wire lead alloy parts on the upper part of a block of electrodes. However, the storage battery of the invention can comprise a light and thin electrode plate because its positive electrode plate does not corrode.

Since electric current flows perpendicular to the wider area surface of the thin collector, the smaller the thickness of the collector is, the smaller is the voltage drop developed when electric current flows perpendicular to the surface of the collector, even if the collector is thin. Thus, even if the weight of the collector is reduced, the resulting output is not lowered. By laminating these cells in sequence, a battery having a higher voltage can be realized, eliminating the necessity of welding or wiring. In other words, if a bipolar battery can be prepared by using the technique of the invention, a very inexpensive battery having a long life and a high energy density can be provided.

[Example 3]

As a result of experiments we have made, it was found that SnO_2 layer formed on the surface of the collector is dissolved with sulfuric acid when a voltage of 1.0 V or less is applied thereto. This potential is reached in the initial stage of formation of the electrode plate during the preparation of lead acid battery. The electrode plate in a lead acid battery shows a voltage as low as 0 to 0.5 V after the injection of sulfuric acid.

In the present invention, when the voltage of the battery was adjusted to 1.0 V or more immediately after

the injection of sulfuric acid, the dissolution of SnO_2 on the surface of the collector was inhibited.

On the other hand, when formation is effected at a high voltage, gas is produced at the surface of SnO_2 during formation, eliminating the adhesivity between the active material and the collector and hence enhancing the internal resistivity of the battery. It was found that the adhesivity between SnO_2 and the active material can be maintained by limiting the voltage during the initial 1 hour of formation to 2 V or less in the invention.

Firstly, SnO_2 was sputtered onto the surface of a pure Pb sheet having a thickness of 0.5 mm to various thicknesses. The coated Pb sheet was then coated with an ordinary active material for lead acid battery to prepare a positive electrode plate. This positive electrode plate was then combined with an ordinary negative electrode plate for lead acid battery and a separator made of microfine glass fibers for valve regulated lead acid battery to prepare a lead acid battery having a capacity of about 0.25 Ah. For comparison, a conventional lead acid battery comprising a conventional positive electrode plate for lead acid battery having no SnO_2 layer formed on the surface of a Pb sheet was prepared and subjected to test.

These batteries were subjected to formation at various voltages for various periods of time after the injection of the electrolyte. These batteries were then each measured for the amount of PbO_2 thus produced by formation. These batteries were each subjected to 120-hour anodization test with a current of 0.05 CA, and then measured for corroded amount. The results were compared. The contents of the test batteries are set forth in Table 2.

The formation was effected in two stages. The first stage involved formation at a restricted voltage.

Table 2: Testing conditions and contents of test batteries

Battery No.	Thickness of SnO ₂ layer (μm)	Time between the termination of injection of electrolyte and the beginning of 1st formation (min)	Voltage of 1st formation (V)	Time required for 1st formation (h)	Conditions of second formation after the termination of 1st formation	Remarks
1	10	0	0.5	0.5, 1, 5	Formed with a current of 0.2 CA until the integrated ampere-hour reaches 350% of the theoretical capacity of positive active material	
2	10	0, 9, 13, 20, 25	1	0.5, 1, 5		
3	10	0	2	0.5, 1, 5		
4	10	0	2.3	0.5, 1, 5		
5	10	0	2.7	0.5, 1, 5		
6	0	120	None	None		Conventional lead acid battery
7	1	0, 9	1	5		
8	3	0, 9, 13	1	5		
9	5	0, 9, 13, 20	1	5		
10	20	0, 9, 13, 20, 25	1	5		

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The results of the foregoing test are described hereinafter. The amount and thickness of PbO_2 layer formed by 1st formation at various voltages for various periods of time in the batteries comprising a positive electrode plate having an SnO_2 layer formed on the surface thereof to a thickness of 10 μm are shown in Figs. 13 and 14. In the present test, the time between the termination of injection of electrolyte and the beginning of formation was 0 minute for all the batteries. As can be seen in Fig. 12, when the voltage of 1st formation was 2 V or less, the amount of PbO_2 was great. The reason for why when the voltage of 1st formation is more than 2 V, the amount of PbO_2 is reduced is presumably that when the initial voltage of formation is too high, gas is violently produced at the interface of SnO_2 with the active material on the surface of the Pb sheet, lowering the efficiency of formation. Further, when the time required for 1st formation was 1 hour or more, the amount of PbO_2 was raised.

As can be seen in the measurements of the corroded thickness after the oxidation test of Fig. 13, when the voltage of 1st formation was less than 1 V, the thickness of corroded layer was the same as that of the conventional lead acid battery comprising no SnO_2 layer formed on the

surface of the collector presumably because the SnO_2 layer was dissolved. However, when formation was effected at a voltage of 1 V or more, there occurred little or no corrosion.

As can be seen in the foregoing results, the voltage of 1st formation should be 1 V or more. Further, in order to increase the amount of PbO_2 , the voltage and time of 1st formation should be 2 V or less and 1 hour or more, respectively.

The relationship among the thickness of SnO_2 layer, the time between the termination of injection of electrolyte and the beginning of formation and the thickness of corroded layer after oxidation test in the case where 1st formation was effected at 1 V for 5 hours is shown in Fig. 15. As can be seen in Fig. 15, when the thickness of SnO_2 layer was raised and the time between the termination of injection of electrolyte and the beginning of formation was reduced, there occurred little or no corrosion during the oxidation rest. On the other hand, when the thickness of SnO_2 layer was reduced or the time between the termination of injection of electrolyte and the beginning of formation was prolonged, there occurred much corrosion after the oxidation test. In order to make clear the conditions under which there

occurs less corrosion, the critical formation time in which corrosion is minimized was replotted versus the thickness of SnO_2 layer in Fig. 16. In order to inhibit the dissolution of SnO_2 layer during formation and hence improve corrosion resistance according to Fig. 16, formation may begin within a period of time T (minute) represented by the following equation after the injection of an electrolyte depending on the thickness of the coat layer of electrically-conductive ceramic (A μm):

$$T \text{ (min.)} \leq 19.2 \log_{10} A \text{ (}\mu\text{m)}$$

In the foregoing Examples, as the substrate for positive collector there was used a metal, i.e., Pb or Ti. However, the substrate for positive collector does not necessarily need to be a metal but may be an electrically-conductive polymer having an electrically-conductive filler incorporated therein. If an electrically-conductive polymer is used as a negative collector as well, a storage battery can be assembled by heat-fusing the positive and negative electrodes to a plastic battery outer case. Thus, no adhesive is required, making it possible to put a cheaper valve regulated lead acid battery to practical use.

<Industrial Applicability>

As mentioned above, the collector coated with the electrically-conductive ceramic of the invention and the storage battery comprising the collector which is kept pressed at a predetermined required pressure and thus requires no connecting parts can give solution to problems with the conventional electrode coated with a thin layer of corrosion-resistant electrically-conductive material that the assembly cost is raised and the adhesivity between the collector and the active material is deteriorated, making it impossible to maintain desired functions or various problems with the conventional lead acid batteries and provide a thin positive collector for lead acid battery having an excellent corrosion resistance and a light weight and a high performance inexpensive lead acid battery having a prolonged life, a high energy density and a high reliability at a low price. Thus, the positive collector for lead acid battery and lead acid battery of the invention have an extremely great industrial value.